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# Dielectric Properties of Water Ice, the Ice Ih/XI Phase Transition and an Assessment of DFT

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## Abstract

The dielectric properties of the hydrogen disordered hexagonal phase (Ih) of water ice have been computed using density functional theory (DFT) based Monte Carlo simulations in the isobaric-isothermal ensemble. Temperature dependent data yield a fit for the Curie-Weiss law of the system and hence a prediction of the temperature of the phase transition from the Ih phase to the hydrogen ordered ice XI phase. Direct simulations around the phase transition temperature confirm and refine the predicted phase transition temperatures and provide data for further properties, such as the linear thermal expansion coefficient. Results have been obtained with both hybrid and semi-local density functionals, which yields insight in the performance of the electronic structure method. In particular, the hybrid functional yields significantly more realistic dielectric constants than the semi-local variant, namely  $\epsilon \approx 116$  as opposed to  $\epsilon \approx 151$  at 273K ( $\epsilon_{\text{experiment}} = 95$ ). This can be attributed to the tendency of semi-local functionals to be biased to configurations with a large dipole moment, and their overestimation of the dipole moments of these configurations. This is also reflected in the estimates of the Ih/XI transition temperature, which is 70-80K and 90-100K for the hybrid and semi-local functional respectively. DFT based sampling of the millions of configurations necessary for this work has been enabled by a Tree Monte Carlo algorithm, designed for massively parallel computers.

**keywords:** Water Ice, Dielectric Properties, Phase Transitions, Density Functional Theory, Monte Carlo

# Introduction

Water ice is a ubiquitous substance and yet despite its familiarity and intensive study for centuries, some of its most basic properties are not fully understood. For example, in the 1850s, Michael Faraday proposed the surface of ice was 'liquid-like'<sup>1</sup>, yet a detailed atomic scale understanding of this structure is still elusive. Below the onset of 'quasi-liquid layer' formation, ice at ambient temperature (ice Ih) is fully crystalline. However, although the water ice surface shows both short and long-range order, it also displays behaviour normally associated with amorphous materials<sup>2</sup>; surface and sub-surface vacancy formation energies, which would expected to be similar, vary by  $\approx 0.8\text{eV}$ , approximately three times the strength of a hydrogen bond. This observation is explicable through consideration of the effects of *orientational disorder* - where a water molecule can adopt one of six possible orientations; the orientational disorder leads to positional disorder of the hydrogen atoms on an ordered oxygen sub-lattice. This disorder contributes to the amazing richness in ice's phase diagram, giving rise to 15 known phases<sup>3</sup>. This hydrogen disorder is the result of a delicate balance between configurational entropy, that has been accurately estimated by Pauling<sup>4</sup> and Giauque<sup>5</sup>, and the small energy differences between the various configurations<sup>6</sup> that respect the Bernal-Fowlers ice rules.<sup>7</sup> This disorder, and the associated fluctuations of the total dipole of the sample, lead to a high dielectric constant for solid water ice Ih ( $\epsilon(272\text{K}) = 95$ ), which is surprisingly similar to that of liquid water ( $\epsilon(278\text{K}) = 86$ ). The term 'dielectric constant' of ice Ih is somewhat imprecise, as the hexagonal symmetry of ice Ih implies that the dielectric tensor will have two unique eigenvalues,  $\epsilon_{\perp}$  and  $\epsilon_{\parallel}$ . The former value is two-fold degenerate, with eigenvectors in the hexagonal plane and orthogonal to the optical axis (also named c or z axis), while the eigenvector corresponding to the latter is parallel to the optical axis of the crystal. Indeed the dielectric anisotropy of ice is exploited in the characterisation of polar ice sheets by radio waves<sup>8</sup> as polycrystalline ice causes a distinct attenuation of radio waves in comparison to oriented ice. If all microscopic configurations of ice were energetically equivalent, as assumed in the Pauling model (see also Minagawa<sup>9</sup>), the anisotropy ( $(\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon_{\parallel}$ ) would be vanishingly small (see e.g. Aragoes *et al.*<sup>10</sup>). Early measurements of this anisotropy, performed by Paul Scherrer

and co-workers in a freezer room of a local brewery in Zurich<sup>11</sup>, yield an anisotropy of 13% near the melting temperature. This value, later confirmed (12%) and extended to a wider temperature range by Kawada<sup>12</sup>, suggests that the precise energetics of these configurations does matter and that the Pauling model is thus not sufficient in this context. The trigger for these experiments at low temperature was his earlier observation<sup>13</sup> of an indication for a phase transition near 70K to what is now known as the proton ordered, ferroelectric, hexagonal phase ice XI.<sup>14</sup> Such a phase transition should be clearly visible in the dielectric properties, as the ordered phase has a low dielectric constant, while the relevant component of the dielectric tensor of the high temperature phase can be approximated by a Curie-Weiss law

$$\epsilon_{\parallel} - \epsilon_{\infty} = A/(T - T_C). \quad (1)$$

where  $A$  is the Curie constant and  $T_C$  the Curie temperature, which should be similar to the phase transition temperature. These experiments are challenging and have lead to a wide range (6K-127K) of estimates for  $T_C$ , as reviewed in Ref.<sup>15</sup>. The origin of this difficulty is the long dielectric relaxation time in pure ice and the slow kinetics of the phase transition, which requires doping with KOH to reduce the associated time-constants from years to more managable values. The uncertain influence of the dopant and the difficulty of growing single crystals containing KOH have made characterization of this phase transition a challenge to experiment. Nevertheless, recent dielectric experiments agree on a phase transition temperature of 72K for H<sub>2</sub>O<sup>16,17</sup> (76K for D<sub>2</sub>O<sup>14</sup>), while thermally stimulated depolarization provides further evidence for ferroelectric ordering<sup>18</sup>, and neutron diffraction has provided the crystal symmetry ( $Cmc2_1$ ) of the ice XI phase<sup>19,20</sup>. The dielectric tensor should thus be considered a quantity that is very sensitive to important aspects of water, namely the polarization of the system, and the detailed energetics of the various hydrogen bonding configurations. The fact that the structure of ice Ih, contrary to that of the liquid (see Ref.<sup>21</sup> for a recent discussion), is well known, also makes the system ideal to quantitatively asses the quality of simulation models. Furthermore, simulation models that reproduce the well

established experimental data, for example the high temperature dielectric tensor, can then be used to investigate more controversial aspects, such as the influence of electrostatic screening between charged defects and orientational (Bjerrum) defects. It is important to recognise that force-field based approaches, including sophisticated high order multipole models cannot currently accurately capture subtle differences in energy between hydrogen orderings. Therefore, quantum mechanical based approaches are essential for benchmarking. Nevertheless, force field based approaches have provided tremendously instructive insights into ice physics. Rick and Haymet proposed a Monte Carlo move suitable for off-lattice calculations of ice<sup>22</sup>, and demonstrated that several non-polarizable empirical atomistic models of water significantly underestimate (by 100%) the dielectric constant of ice. This result was later verified and extended by several other groups<sup>10,23,24</sup>. Adding polarizability to the model improved results significantly, which was attributed to the larger molecular dipole in these models.<sup>22</sup> However, none of the methods displayed a significant anisotropy of the dielectric tensor, as observed experimentally, which may be related to the fact that these models predict an anti-ferroelectric ordered phase to be more stable than the experimental ferroelectric phase.<sup>10,22,24</sup> In fact, Hirsch and Ojamäe found<sup>6</sup> an almost anti-correlation between the energies computed with DFT and empirical methods for the sixteen unique proton ordered configurations compatible with an orthorhombic unit cell containing eight water molecules, which has been attributed to incorrect higher order electrostatic multipoles in the empirical force fields<sup>25</sup>. Furthermore, HF and DFT yield (independent of the density functional employed), a lowest energy configuration that is indeed ferroelectric<sup>6,25-28</sup>, indicating that these methods might be capable of reproducing the fine energy details in this system. Singer and co-workers parametrized an analytical model based on graphs, i.e. hydrogen bond network patterns, to DFT (BLYP) reference values, and with this approach, were able to perform Monte Carlo simulations that predict the phase transition temperature between Ih and XI to be 98K in good agreement with experiment.<sup>26,29</sup> This is a very interesting and powerful approach, but is probably limited to models containing less than  $\approx 60$ -70 molecules, because of the combinatorial explosion of enumerating possible hydrogen bonding arrangements. In addition, the model may not be easily extended to consider orientational (Bjerrum)

or ionic defects (i.e. hydronium and hydroxide). Unfortunately, the dielectric properties were not reported, so cross validating the employed model directly is not possible. In all simulations discussed here, nuclear quantum effects, which are relatively small in this context, have not been taken into account, and hence comparison with results for D<sub>2</sub>O, which is the more 'classical' isotope, will be considered whenever possible. Rusnak and co-workers estimated the static dielectric constants of liquid water and ice for PBE, using a free energy perturbation approach that employs a classical potential to sample configurations, which are reweighted to *ab initio* values.<sup>30</sup> However, obtained results underestimate the experimental value significantly ( $\epsilon(253K) = 67$ ). This difference might in part be due to their use of a Bader-like analysis to obtain molecular dipoles, instead of relying on the modern theory of polarization.<sup>31,32</sup> The latter theory was employed in the simulations of Sharma *et al.* to compute the dielectric constant of liquid water.<sup>33</sup> Based on a 20ps simulation of liquid water with the PBE functional in the canonical ensemble (NVT), a value in surprisingly good agreement with experiment was obtained ( $\epsilon(330K) = 67$  vs.  $\epsilon(330K) = 68$ ). For ice Ih, the proton configurations could not be sampled, but a molecular dipole derived from a representative ice configuration (3.32D), in good agreement with experiment would be obtained for a plausible angular correlation factor  $G_K \approx 2.55$ . It is noteworthy that the same correlation factor obtained by commonly used empirical potentials varies in the range 1.34-2.7.<sup>10</sup>

In the current work, the merits of the various approaches mentioned above have been combined, and explicit sampling of hydrogen disorder at the DFT level is employed to 1) compute the dielectric tensor at various temperatures using the modern theory of polarization, 2) to determine the Ih/XI phase transformation temperature directly, and 3) to assess the quality of semi-local and hybrid density functional theory for water ice.

## Computational methods

Calculations have been performed with the free simulation package CP2K/Quickstep<sup>34,35</sup> that has been enhanced with a Monte Carlo (MC) algorithm, named Tree Monte Carlo (TMC). The

system studied consists of 96 water molecules in an orthorhombic cell, initially  $13.57\text{\AA} \times 15.67\text{\AA} \times 14.73\text{\AA}$ . This cell is sufficiently large to allow for a Gamma-point calculations, and is similar in size to the classical model systems employed previously (e.g. 128 molecules in Ref.<sup>22</sup>). Near the phase transition temperature, size effects can not be excluded. Monte Carlo simulations have been performed in the isobaric-isothermal (NPT) ensemble<sup>36</sup> at 1 bar, except when the canonical (NVT) ensemble is mentioned explicitly. DFT calculations are based on the semi-local functionals by Perdew, Burke, and Ernzerhof (PBE)<sup>37</sup> and by Becke, Lee, Yang and Parr (BLYP)<sup>38,39</sup> and the corresponding hybrid functionals PBE0<sup>40</sup> and B3LYP<sup>39,41,42</sup>. The latter two functionals contain a fraction of Hartree-Fock exchange (denoted HFX), 25% and 20% respectively, and are thus non-local. All functionals are combined with a dispersion correction by Grimme (which we denote D2)<sup>43</sup>, which is essential to obtain a qualitatively correct density of liquid water in NPT simulations.<sup>44</sup> Norm-conserving Goedecker-Teter-Hutter (GTH)<sup>45</sup> pseudopotentials are employed together with a triple-zeta valence basis set and two polarization functions (TZV2P). HFX is computed with a robust gamma-point implementation<sup>46,47</sup> using a truncation radius of  $6\text{\AA}$ , and the Auxiliary Density Matrix Method (ADMM) with the pFIT3 basis.<sup>48</sup> Periodic boundary conditions have been used throughout, and electrostatics are computed using an Ewald-sum. This implies so called conducting or tin-foil boundary conditions<sup>49</sup>, suitable for samples embedded in a medium of high dielectric constant, and is equivalent to enforcing closed circuit electrical boundary conditions without applied bias.<sup>50</sup> These boundary conditions are almost always applied in electronic structure calculations and typically used in force field based simulation of ice (see e.g.<sup>10,22,24</sup>). The plane wave cutoff was 800 Ry for NPT and 400 Ry for NVT calculations, with the number of grid points kept fixed during NPT simulations.<sup>35,51</sup>

The elements of the dielectric tensor are obtained as the second moments of the dipole distribution using

$$\epsilon_{\alpha\beta} = \epsilon_{\infty} + \left( \frac{4\pi}{3Vk_B T} \right) (\langle \mathbf{M}_{\alpha} \cdot \mathbf{M}_{\beta} \rangle - \langle \mathbf{M}_{\alpha} \rangle \langle \mathbf{M}_{\beta} \rangle), \quad (2)$$

where  $\mathbf{M}_{\alpha}$  is the component of the total cell dipole in the  $\alpha$  direction, and  $\epsilon_{\infty}$  is the optical dielectric constant, taken to be one in the following, and  $\langle \cdot \rangle$  denotes ensemble averaging. In the context



of periodic DFT, changes in the cell dipole are obtained from the Berry phase formulation of polarization<sup>31</sup>.

Monte Carlo generates a sequence of configurations, a Markov chain, that samples a given ensemble based on acceptance/rejection of random configurational changes (moves). Three important strengths of Monte Carlo are exploited in the context of this study. First, in addition to the traditional moves (atom and molecule translation, molecule rotation, and non-isotropic volume changes), a proton reordering move is employed<sup>22</sup>. This specialized move allows for re-orienting several molecules in a closed loop of hydrogen bonded neighbors in a way that obeys the Bernal-Fowler ice rules and may change the effective dipole of the unit cell, circumventing the high energy barriers that the physical process must overcome in experiment or unbiased molecular dynamics simulations. Second, in the context of DFT it is advantageous to employ a pre-sampling strategy in which a sub-Markov chain is generated with an approximate classical potential.<sup>51–53</sup> In this nested MC approach, the entire sub-Markov chain is accepted/rejected with a single DFT calculation, leading to exact sampling of the DFT potential at much reduced computational cost. Note that converged MC results are independent of the approximate classical potential, but the rate of convergence depends on the quality of the approximation. Here a refitted classical non-polarizable potential based on the model from Ref.<sup>54</sup> has been employed, which provides good acceptance. In our current approach, 50 (NPT) or 100 (NVT) nested MC moves are applied, which are constrained to a fixed sub-cell with edges of length 8Å in order to retain sufficiently large acceptance rates in the DFT step. This nested MC setup leads to a high fraction of the DFT calculations being employed to accept/reject hydrogen reordering moves, resulting in effective sampling of the cell dipole. Third, Monte Carlo contains an intrinsic parallelism that has so far not yet been exploited in molecular simulation, but is here used by the TMC algorithm for obtaining long Markov chains on massively parallel computers. It is based on the observation that new (future) configurations in the Markov chain can be constructed on the fly and instantaneously, before the energy of the current configuration has been evaluated, as neither energy nor forces are required for the MC moves.<sup>55</sup> This approach requires speculation on the outcome of the acceptance check, or when used in a systematic fashion, builds a tree of

configurations assuming both possible outcomes of this check. All the configurations present in the tree can be computed simultaneously, limited only by the available resources. Finally, the Markov chain, identical to the conventional serial one, is constructed, discarding the configurations that are off the chain, as the energies become available. The implementation of this algorithm, which includes a number of techniques to reduce the amount of discarded work, is freely available<sup>34</sup> and will be discussed in more detail elsewhere. TMC has been key to reduce the wall time per generated Markov chain element to 2.5 s and 14 s for PBE and PBE0 respectively, and ultimately allowed for single MC chains with nearly a million moves.

## Results and discussion

**Table 1: Elements of the dielectric tensor and dielectric anisotropy obtained with PBE-D2 and PBE0-D2 in NPT ensemble. The difference between  $\epsilon_{xx}$ ,  $\epsilon_{yy}$  and  $\epsilon_{\perp} = (\epsilon_{xx} + \epsilon_{yy})/2$  is used as an estimate of the statistical uncertainty.**

	T[K]	$10^5$ MC moves	$\epsilon$	$\epsilon_{\perp}$	$\epsilon_{\parallel}$	$(\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon_{\parallel}$
PBE0-D2	273	7.6	116	$108 \pm 3$	131	17%
PBE0-D2	150	8.6	266	$234 \pm 0$	331	30%
PBE-D2	273	10.1	151	$139 \pm 7$	174	20%
PBE-D2	200	8.3	238	$202 \pm 7$	310	35%
PBE-D2	150	8.4	366	$298 \pm 28$	502	41%

The temperature dependent dielectric constant of ice Ih at ambient pressure is a central result of this work. It is a challenging quantity to obtain by simulation, as extensive sampling is necessary for convergence. However, provided 100000s of MC steps are performed, convergence can be reached even with first principles simulations. This is demonstrated for five MC simulations in the NPT ensemble, based on either the PBE-D2 or PBE0-D2 functional, in the upper panel of Fig. 1. The relevant components of the dielectric tensor obtained by these simulations are summarized in Table 1. This data clearly shows that  $\epsilon$  obtained with PBE-D2 is significantly larger than the one obtained with PBE0-D2. At the melting point,  $\epsilon(273K) = 116$  is in fair agreement with the experimental result of Johari *et al.*<sup>15</sup>  $\epsilon(273K) = 95$ , while PBE-D2 significantly overestimates it ( $\epsilon(273K) = 151$ ). The origin of this difference is related to the nature of the density functionals,

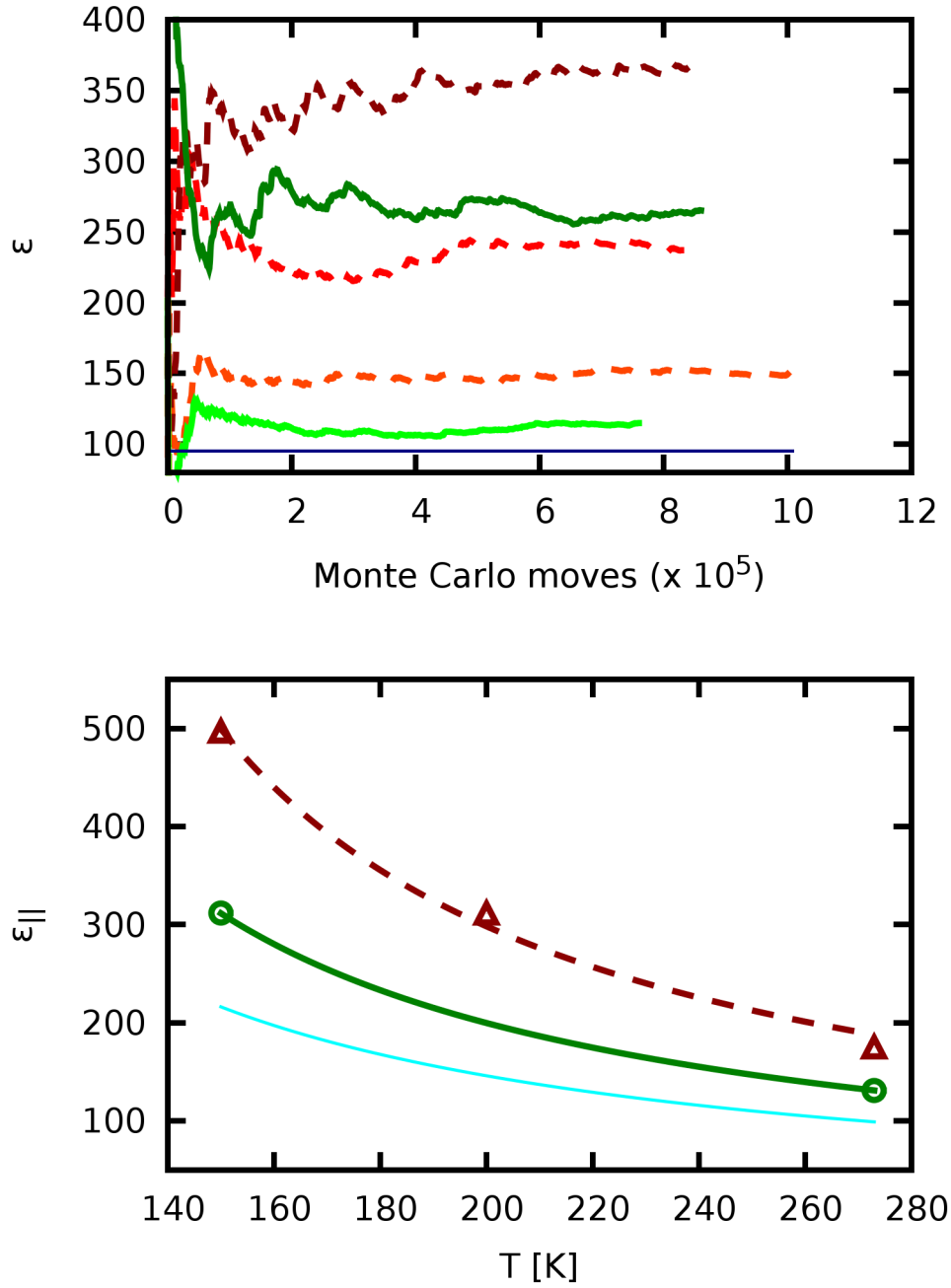


Figure 1: upper panel: Shown are the running averages of  $\epsilon$  for PBE-D2 at 273K (orange), 200K (red), 150K (brown) and PBE0-D2 at 273K (lightgreen) and 150K (green). The experimental value of Johari<sup>15</sup> at 273K is shown in blue. lower panel: Shown are the converged values of  $\epsilon_{\perp}$  for PBE0-D2 (circles) and PBE-D2 (triangles), with the corresponding fit (solid lines) of Curie-Weiss law (1). Experimental data of Kawada *et al.*<sup>16</sup> (light blue) are shown for comparison.

as we discuss in more detail below. Of particular interest is the value of the dielectric anisotropy  $((\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon_{\parallel})$ , because it is indicative of the XI/Ih phase transition. Simulations based on empirical force fields predict very small or zero values of the anisotropy.<sup>10,22,24</sup> PBE0-D2 calculations at 273K result in an anisotropy value of 18%, which is slightly greater than the measured value of approximately 12% of Kawada *et al.*<sup>12</sup>. PBE-D2 overestimates the anisotropy more significantly (22%), indicative of a bias towards configurations that display a large dipole along the  $\parallel$  direction. Note that, the average *molecular* dipole moments found for apolar ice slabs computed with PBE were approximately 10% greater than PBE0<sup>2</sup> which contributes to the observed difference in anisotropy using the semi-local and hybrid functionals. As the temperature decreases and the Ih/XI phase transition temperature approaches, the anisotropy becomes larger. A fit of the Curie-Weiss law through the simulation data, shown in the lower panel of Fig. 1 yields  $T_C = 60\text{K}$  and  $T_C = 79\text{K}$  for PBE0-D2 and PBE-D2, respectively. However, given the limited data, the uncertainty in this fit is likely large, on the order of 10K. Furthermore, a true divergence as described by equation Eq. 1 can not be observed due to finite size effects. Nevertheless, the Curie temperatures found are close to the experimental phase transition temperature; 72K for H<sub>2</sub>O and 76K for D<sub>2</sub>O.

Based on these estimates, the phase transition temperature has been determined by direct simulation. In particular, NPT MC runs at various temperatures between 50 and 100K have been started from the same ice Ih configuration, and run for at least 250000 MC steps. As shown in Fig. 2, this leads to a spontaneous phase transformation to the expected ice XI phase for the low temperatures, while the systems at the higher temperatures remain in the ice Ih phase. The resulting phase transition temperatures can thus be bracketed by 70-80K (PBE0-D2) and 90-100K (PBE-D2), in fair agreement with the estimates derived from the Curie-Weiss fit. The PBE-D2 result is in agreement with the 98K computed by a graph based model parametrized to the semi-local BLYP functional, yielding additional support for this approach.<sup>26,29</sup> Nevertheless, the PBE0-D2 model can be assumed to be the most predictive, given its favorable comparison to dielectric experimental data, obtained with well established experiments near the melting point. Furthermore, the fact that the transition temperature is relatively insensitive to the precise DFT model suggests that this prediction

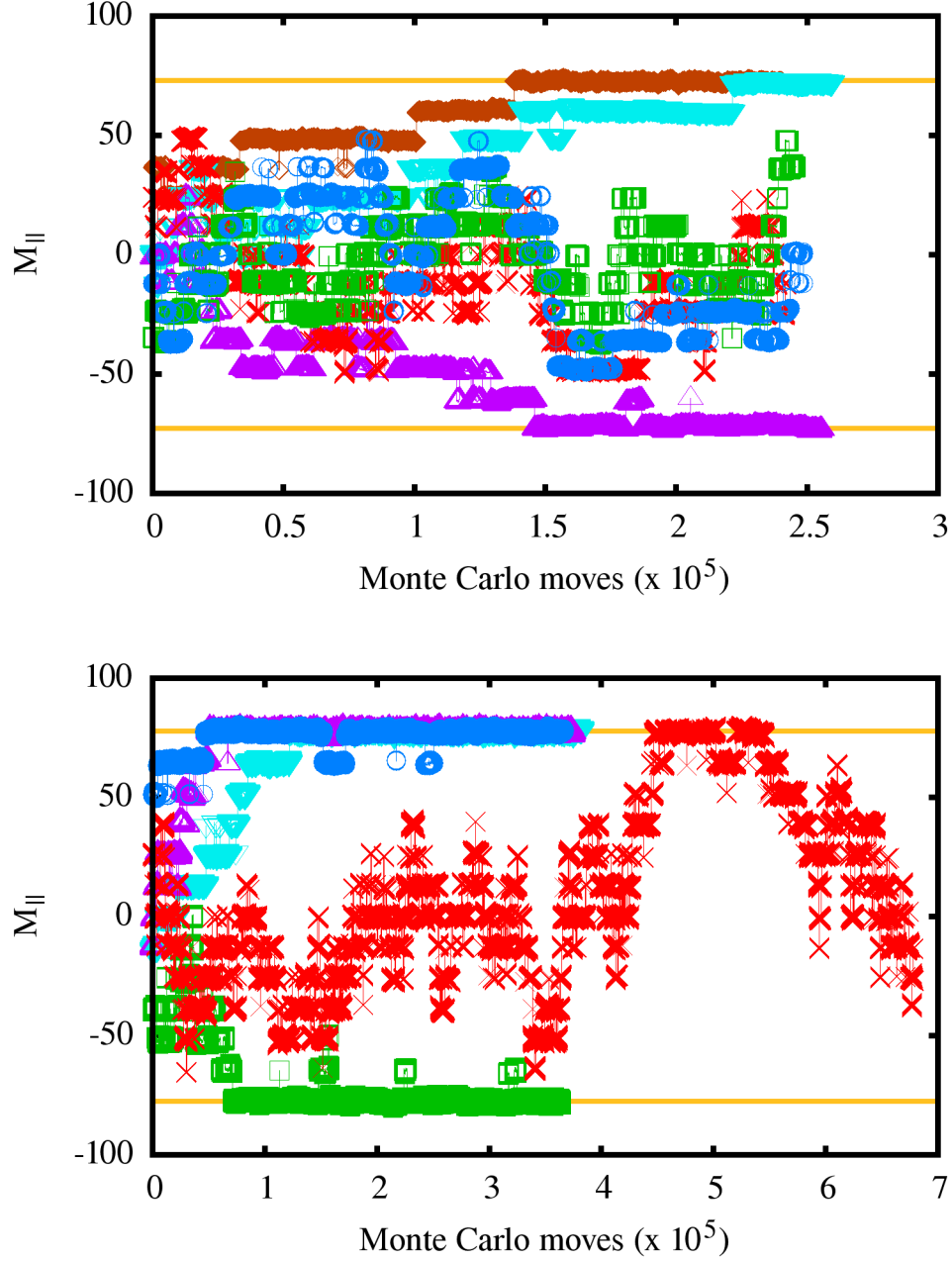


Figure 2: Evolution of the z component of the total cell dipole for NPT calculations at various temperatures. upper panel: PBE0-D2, lower panel: PBE-D2. The different colors and symbols correspond to 100K (red, crosses), 90K (green, squares), 80K (blue, circles), 70K (violet, triangles up) and 60K (light blue, triangles down) and 50K (brown, diamonds). The solid (orange) lines indicate the permanent dipole of the ice XI phase.

will be robust.

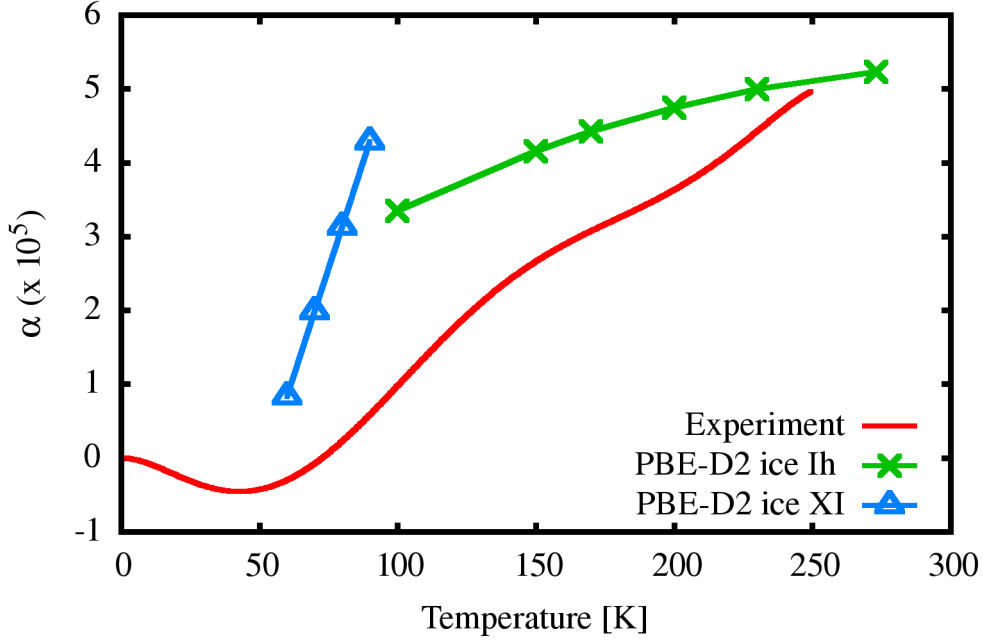


Figure 3: Linear expansion coefficient  $\alpha$ , fitted using NPT ensembles calculated with and PBE-D2 functionals for ice Ih phase (crosses) and ice XI phase (triangles), compared with experimental results of D<sub>2</sub>O of Röttger<sup>56</sup> (solid red line)

The advantage of direct MC simulation of a reliable atomistic model is that further properties can be obtained from the generated trajectories. Here we investigate the temperature dependent density, or equivalently the volume, given its relevance for  $\varepsilon$  (see below) and the fact that this quantity is directly accessible from the NPT simulations performed. Indeed, NPT simulations employ a flexible simulations cell, which fluctuates around a temperature dependent average value ( $\sigma(273K) \approx 0.12\text{\AA}$  for our simulation cell). At the melting point, both models overestimate the density, with 0.960 and 0.995  $g/cm^3$  for PBE0-D2 and PBE-D2 respectively, compared to the experimental results obtained by Röttger<sup>56</sup> (0.917  $g/cm^3$ ). PBE0-D2 is again the best model, with a volume that is underestimated by 4.5 %. The temperature dependence of the volume can be described by the linear thermal expansion coefficient  $\alpha(T)$  defined by

$$\alpha(T) = \frac{1}{3} \frac{1}{V(T)} \frac{\partial V(T)}{\partial T}. \quad (3)$$

Only for PBE-D2 are sufficient data available to yield a stable polynomial fit of the temperature dependence of the volume, using a third order polynomial for the ice Ih phase (100-273K) and a second order polynomial for the ice XI phase (60-90K). In Fig 3, the corresponding  $\alpha(T)$  is compared to the experimental results by Röttger<sup>56</sup>. Given the slow kinetics of the XI/Ih phase transition, it is reasonable to assume that the experimental system consists of a mixture of both phases<sup>57</sup>, with a precise constitution that depends on the preparation method. Indeed, ice XI has never been reported to have been made more than 70% pure.<sup>14</sup> It is therefore reasonable to assume that the experimental curve can be approximated by a combination of the simulation data of the pure phases, which suggests good qualitative agreement. In particular, for even lower temperatures, a negative thermal expansion coefficient could be expected.

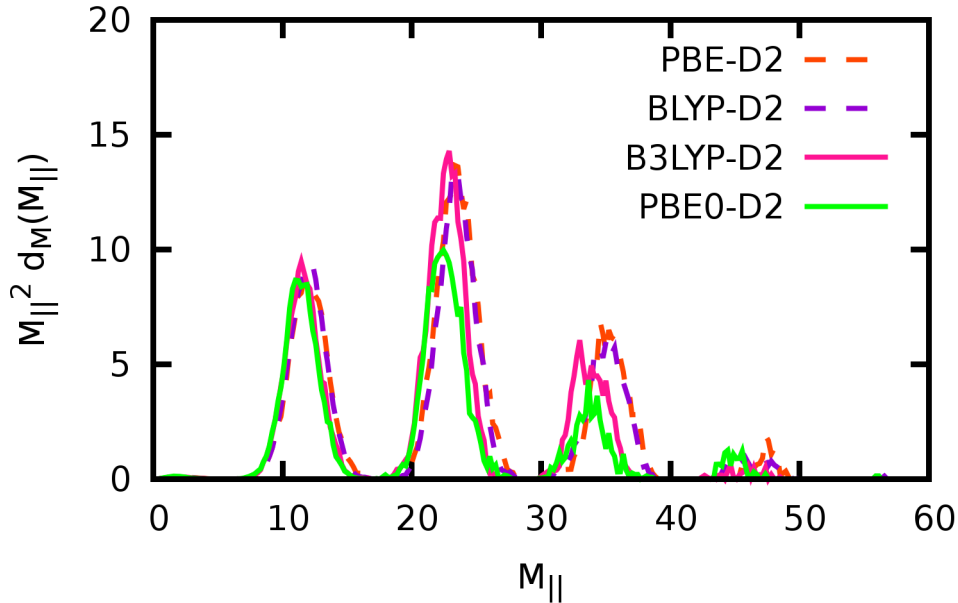


Figure 4: Distribution of the z component of the dipole moment, weighted by the dipole squared. This weighting corresponds to the contribution of these peaks to  $\epsilon$ . Results have been computed for semi-local (PBE-D2 and BLYP-D2) and hybrid (B3LYP-D2 and PBE0-D2) functionals in the NVT ensemble at 273K.

Finally, we show that the observed differences between PBE-D2 and PBE0-D2 are more general in nature. To do so, we have performed MC simulations at constant volume (NVT), 273K and experimental density, and compared two pure DFT (PBE-D2 and BLYP-D2) and two hybrid

**Table 2: Elements of the dielectric tensor and the dielectric anisotropy obtained in the NVT ensemble at 273K and experimental density with the PBE-D2, PBE0-D2, BLYP-D2 and B3LYP-D2 functionals. To illustrate the effect of compression, one additional NVT result at 106% of the density is provided for PBE-D2.**

	T[K]	$10^5$ MC moves	$\epsilon$	$\epsilon_{\perp} \pm \frac{(\epsilon_{xx}-\epsilon_{yy})}{2}$	$\epsilon_{\parallel}$	$(\epsilon_{\parallel} - \epsilon_{\perp})/\epsilon_{\parallel}$
Exp. (Ref. <sup>15</sup> )	273		95			
Exp. (Ref. <sup>12</sup> )	273		90	87	99	12%
PBE-D2	273	6.9	127	$114 \pm 2$	152	25%
PBE-D2 (106%)	273	3.2	145	$126 \pm 3$	183	31%
PBE0-D2	273	2.8	103	$98 \pm 4$	112	12%
BLYP-D2	273	13.7	122	$110 \pm 1$	144	24%
B3LYP-D2	273	3.2	110	$98 \pm 1$	133	26%

(B3LYP-D2 and PBE0-D2) functionals. The data for these simulations is summarized in Table 2. Constant volume simulations facilitate the comparison between the functionals, and can be used to highlight the importance of employing the NPT ensemble for the calculation of the dielectric constant. In particular, the PBE-D2 simulations have been performed at 100% and 106% of the experimental density, the latter being similar to the equilibrium density of the PBE-D2 functional. While the latter simulation yields  $\epsilon = 145$ , very similar to the NPT results of  $\epsilon = 151$ , the simulation at experimental density yields  $\epsilon = 127$ , a significant reduction of the value. Compared to the NPT simulations, a similar reduction is also observed for PBE0-D2, which at experimental density provides an even better estimate of  $\epsilon$  (103) and anisotropy (12%). This sensitivity of  $\epsilon$  to the density (volume), suggests that modifications to the functional that improve the lattice parameters could yield enhanced dielectric properties. At the same density, the overestimation of  $\epsilon$  in the case of semi-local functionals is due to two effects, visible in Fig. 4. These effects are more important than the small differences in geometry between semi-local and hybrid functionals (e.g.  $r_{OH} = 1.000$  and  $r_{OH} = 0.985$  respectively). First, as can be seen as a shift of the position of the peaks, dipoles of a given configuration are enhanced by roughly 5%. Second, visible by the area under the peaks, these polarized configurations are sampled more often, i.e. are energetically favorable. Both effects are consistent with the overestimation of polarizability by semi-local density functionals (see also Ref.<sup>2</sup>) and with the improvements expected for a hybrid functional.<sup>58</sup> Ultimately, this is a result of



the underestimation of the band gap by semi-local functionals, a deficiency that is, also in water ice, significantly improved by hybrid functionals.<sup>28</sup>

## Conclusion

The temperature dependent dielectric constant of ice Ih contains a wealth of information about the interactions between water molecules. It contains the most visible signature of the Ih/XI phase transition, which is the result of a delicate balance between energy and entropy. Here, this property has been computed directly from extensive sampling of hybrid and semi-local DFT models in the appropriate ensemble. We find that semi-local DFT significantly overestimates the dielectric constant ( $\epsilon(273K) \approx 150$  for PBE-D2), whereas hybrid density functionals ( $\epsilon(273K) \approx 116$  for PBE0-D2) provide better agreement with experiment ( $\epsilon(273K) \approx 95$ ). The electronic overpolarization and the energetic bias towards configurations with large dipole both contribute to the error observed for the semi-local functional. This effect is also observed for a different family of functionals (BLYP-D2 and B3LYP-D2), and is thus likely of general nature. Furthermore, we expect that this error will also be present in the liquid phase, which could have implications for example for simulations of the behavior of water near (electrified) interfaces, or for the solvation and interaction of ions including incipient species such as the Zundel ion and processes involving proton transport. The Ih/XI phase transition temperature has been determined both from a Curie-Weiss fit and from direct MC simulations for both PBE0-D2 and PBE-D2. All these values are in good agreement, lending support to our methodology, and yield a transition temperature of 70-80K (PBE0-D2) or 90-100K (PBE-D2). Given the validation of our model via the dielectric constant, we expect the PBE0-D2 model to be most predictive. This PBE0-D2 result confirms accurately the measurements by Kawada (Ref.<sup>16</sup>) and thus suggests that the experimental procedure of KOH doping can indeed be used to accelerate the kinetics of the Ih/XI phase transformation without influencing the final equilibrium structure formed. Finally, MC sampling of explicit atomistic models yields data that can be used to compute several properties, and as an example, the linear thermal expansive coefficients

of ice Ih and XI has been reported in their respective temperature ranges. This shows that the steady increase in computer power and the development of novel algorithms have made the extensive sampling of disordered solids at the DFT level possible, and that this approach can now be used to evaluate properties that have long challenged experiment and theory alike.

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## TOC Graphic

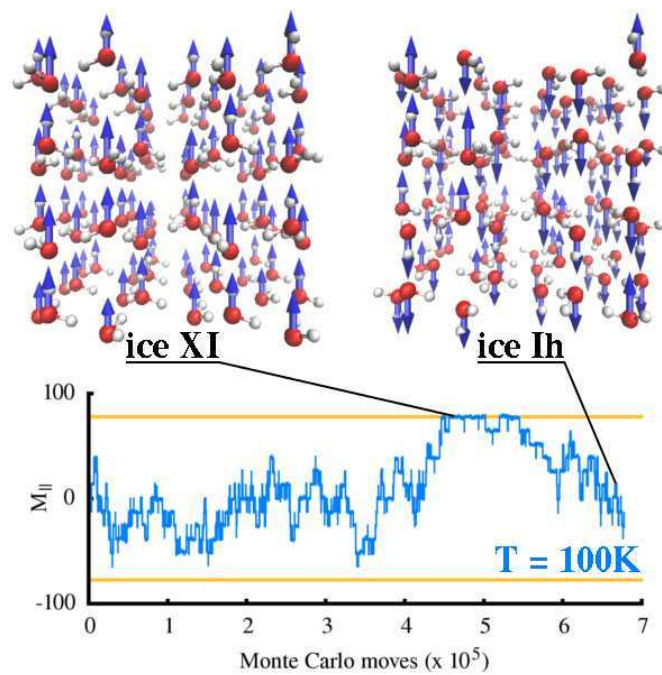


Figure 5: For Table of Contents Use Only